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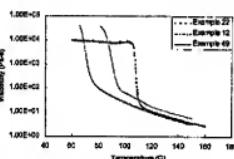
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(54) Title: MULTIPLE CATALYST SYSTEM FOR OLEFIN POLYMERIZATION AND POLYMERS PRODUCED THEREFROM



WO 2004/046214 A2



(57) Abstract: This invention relates to a polymer comprising one or more C3 to C40 olefins, optionally one or more diolefins, and less than 1.5 mole % ethylene, where the polymer has: a) a Dot T-Peel of 1 Newton or more; and b) a branching index (g') of 0.95 or less measured at the Mz of the polymer; c) an Mw of 100,000 or less. This invention also relates a polymer comprising one or more C3 to C40 olefins where the polymer has: a) a Dot T-Peel of 1 Newton or more on Kraft paper; b) a branching index (g') of 0.95 or less measured at the Mz of the polymer; c) a Mw of 10,000 to 100,000; and d) a heat of fusion of 1 to 70 J/g. This invention also relates a polymer comprising one or more C3 to C40 olefins where the polymer has: a) a Dot T-Peel of 1 Newton or more on Kraft paper; b) a branching index (g') of 0.98 or less measured at the Mz of the polymer; c) a Mw of 10,000 to 60,000; d) a heat of fusion of 1 to 50 J/g. This invention also relates to a homopolypropylene or a copolymer of propylene and up to 5 mole % ethylene having: a) an isotactic run length of 1 to 30 (isotactic run length "IRL" is defined to be the percent of minimum pentad divided by 0.5 x percent of mmmeptad) as determined by Carbon 13 NMR, preferably 3 to 25, more preferably 4 to 20, b) a percent of t dyad of greater than 20%, preferably from 20 to 70% as determined by Carbon 13 NMR, and c) a heat of fusion of 70 J/g or less, preferably 60 J/g or less, more preferably between 1 and 55 J/g, more preferably between 4 and 60 J/g. This invention further relates to a process to produce an olefin polymer comprising: 1) selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a crystallinity of 5% or less at selected polymerization conditions; 2) selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 20% or more at the selected polymerization conditions; 3) contacting the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, at the selected polymerization conditions in a reaction zone; 4) obtaining the polymer. This invention further relates to a continuous process to produce a branched olefin polymer comprising: 1) selecting a first catalyst component capable of producing a polymer having an Mw of 1000,000 or less and a crystallinity of 5% or less under selected polymerization conditions; 2) selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 20% or more at the selected polymerization conditions; 3) contacting the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, and, optionally one or more diolefins; 4) at a temperature of greater than 100 °C; 5) at a residence time of 120 minutes or less; 6) wherein the ratio of the first catalyst to the second catalyst is from 1:1 to 50:1; 7) wherein the activity of the catalyst components is at least 100 kilograms of polymer per gram of the catalyst components; and wherein at least 20% of the olefins are converted to polymer.



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**Multiple Catalyst System for Olefin
Polymerization and Polymers Produced Therefrom**

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Related Case Information

[0001] This application claims priority to provisional USSN 60/418,482, filed October 15, 2002, entitled "Multiple Catalyst System for Olefin Polymerization and Polymers Produced Therefrom." This application also claims priority from USSN 60/460,714, filed April 4, 2003 entitled "Polyolefin Adhesive Compositions and Articles Made Therefrom."

[0002] This application is related to USSN 60/199,093, filed on April 21, 2000 and US2000000199093P, filed April 20, 2001 claiming priority from USSN 60/199,093. The instant application also relates to USSN 60/171,715, filed December 21, 1999; USSN 09/745,394, filed December 21, 2000; and USSN 09/746,332 filed December 21, 2000. The instant application also relates to WO 01/81493.

Field of the Invention

[0003] This invention relates to a process to polymerize olefins using multiple catalysts and polymers produced therefrom. In particular this invention relates to a process to produce polyolefin adhesives and the adhesives so produced.

Background of the Invention

[0004] For some applications such as adhesives individual polymers do not possess the necessary combination of properties. Individual polyolefins having certain characteristics are often blended together in the hope of combining the positive attributes of the individual components. Typically the result is a blend which displays an average of the individual properties of the individual resins. For example EP 0 527 589 discloses blends of flexible, low molecular weight amorphous polypropylene with higher molecular weight isotactic polypropylene to obtain compositions with balanced mechanical strength and flexibility. These compositions show better flexibility compared to that of the isotactic polypropylene alone, but are still lacking in other physical attributes. Physical blends also have the problems of inadequate miscibility. Unless the components are selected for their compatibility they can phase separate or smaller components can migrate to the surface. Reactor blends, also called intimate blends (a composition comprising two or more polymers made in the same reactor or in a series of reactors) are often used to address these issues, however finding catalyst systems that will operate under the same environments to produce different polymers has been a challenge.

[0005] Multiple catalyst systems have been used in the past to produce reactor blends (also called intimate blends) of various polymers and other polymer compositions. Reactor blends and other one-pot polymer compositions are often regarded as superior to physical blends of similar polymers. For example US 6,248,832 discloses a polymer composition produced in the presence of one or more stereospecific metallocene catalyst systems and at least one non-stereospecific metallocene catalyst system. The resultant polymer has advantageous properties over the physical blends disclosed in EP 0 527 589 and US 5,539,056.

[0006] Thus there has been interest in the art in developing multiple catalyst systems to produce new polymer compositions. For example, US Patent 5,516,848 discloses the use of two different cyclopentadienyl based transition metal compounds activated with alumoxane or non-coordinating anions. In particular, the examples disclose, among other things, catalyst compounds in combination, such as $(Me_2Si(Me_4C_9)(N-c-C_{12}H_{21})TiCl_2$ and rac- $Me_2Si(H_4Ind)ZrCl_2$, or $Me_2Si(Me_4C_9)(N-c-C_{12}H_{21})TiCl_2$ and $Me_2Si(Ind_2)HfMe_2$, (Ind = indenyl) activated with activators such as methylalumoxane or N,N-dimethyl anilinium tetrakis(pentafluorophenyl) borate to produce polypropylenes having bimodal molecular weight distributions (Mw/Mn), varying amounts of isotacticity (from 12 to 52 weight % isotactic PP in the product in Ex 2, 3 and 4), and having weight average molecular weights over 100,000, and some even as high as 1,200,000 for use as thermoplastics. Likewise, US 6,184,327 discloses a thermoplastic elastomer comprising a branched olefin polymer having crystalline sidechains and an amorphous backbone wherein at least 90 mole percent of the sidechains are isotactic or syndiotactic polypropylene and at least 80 mole percent of the backbone is atactic polypropylene produced by a process comprising: a) contacting, in solution, at a temperature from about 90°C to about 120°C, propylene monomers with a catalyst composition comprising a chiral, stereorigid transition metal catalyst compound capable of producing isotactic or syndiotactic polypropylene; b) copolymerizing the product of a) with propylene and, optionally, one or more copolymerizable monomers, in a polymerization reactor using an achiral transition metal catalyst capable of producing atactic polypropylene; and c) recovering a branched olefin polymer. Similarly US 6,147,180 discloses the synthesis of a thermoplastic polymer composition, which is produced by first polymerizing monomers to produce at least 40% vinyl terminated macromonomers and then copolymerizing the macromonomers with ethylene. In addition US 6,323,284 discloses a method to produce thermoplastic compositions (mixtures of crystalline and amorphous polyolefin copolymers) by

copolymerizing alpha-olefins and alpha, omega dienes using two separate catalyst systems.

[0007] Likewise others have experimented with multiple stage processes to produce new polymer compositions. For example EP 0 366 411 discloses a graft polymer having an EPDM backbone with polypropylene grafted thereto at one or more of the diene monomer sites through the use of a two-step process using a different Ziegler-Natta catalyst system in each step. This graft polymer is stated to be useful for improving the impact properties in blended polypropylene compositions.

[0008] Although each of the polymers described in the above references has interesting combinations of properties, there remains a need for new composition that offer other new and different property balances tailored for a variety of end uses. In particular, it would be desirable to find a composition that is strong yet has adhesive characteristics and the ability to be applied using adhesive technology and equipment.

[0009] For general information in this area, one may refer to:

1. DeSouza and Casagrande, in 2001 addressed the issue of binary catalyst systems in "Recent Advances in Olefin Polymerization Using Binary Catalyst Systems, Macromol. Rapid Commun. 2001, 22, No. 16 (pages 1293 to 1301). At page 1299 they report propylene systems that produce a "gooey" product.
2. Studies with respect to the production of stereoblock polypropylene by using in-situ mixtures of metallocene catalysts with different stereoselectivity were recently performed by Lieber and Brintzinger in "Propene Polymerization with Catalyst Mixtures Containing Different

Ansa-Zirconocenes: Chain Transfer to Alkylaluminum Cocatalysts and Formation of Stereoblock Polymers", *Macromolecules* 2000, 33, No.25 (pages 9192-9199). Propylene polymerization reactions were performed using metallocene catalysts $H_4C_2(Flu)_2ZrCl_2$, *rac*- $Me_2Si(2-Me-4-tBu-C_2H_2)_2ZrCl_2$ and *rac*- $Me_2Si(2-MeInd)_2ZrCl_2$ in the presence of either MAO (methylalumoxane) or triisobutylaluminium (Al^tBu_3) /triphenylcarbenium tetrakis(perfluorophenylborate) (trityl borate) as the cocatalyst. Propylene polymerization using the mixed catalysts, $H_4C_2(Flu)_2ZrCl_2$ and $Me_2Si(2-MeInd)_2ZrCl_2$ in the presence of either MAO or Al^tBu_3 /trityl borate produced waxy solids, which are completely separable into an atactic (diethyl ether-soluble) and an isotactic (insoluble) fraction. Neither fraction contained any combination of isotactic and atactic pentad patterns indicating that these catalyst mixtures did not form stereoblock polymers.

3. Aggarwal addressed the various polymers produced in "Structures and Properties of Block Polymers and Multiphase Polymer Systems: An Overview of Present Status and Future Potential", S. L. Aggarwal, Sixth Biennial Manchester Polymer Symposium (UMIST Manchester, March 1976)
4. "Selectivity in Propene Polymerization with Metallocene Catalysts" Resconi, et al, *Chem Rev.* 2000, 100, 1253-1345.

[0010] None of the references above has directly addressed the need for polyolefin based adhesives containing both amorphous and crystalline components. Such adhesives are desired in the industry as a replacement for blends requiring significant amount of hydrocarbon resin tackifiers.

[0011] Additional references that are of interest include:

- 1) EP Patents: EP 0 619 325 B1, EP 719 802 B1;

- 2) US Patents/Publications: 6,207,606, 6,258,903; 6,271,323; 6,340,703, 6,297,301, US 2001/0007896 A1, 6,184,327, 6,225,432, 6,342,574, 6,147,180, 6,114,457, 6,143,846, 5,998,547; 5,696,045; 5,350,817, US 6,569,965,
- 3) PCT Publications: WO 00/37514, WO 01/81493, WO 98/49229, WO 98/32784; and WO 01/09200
- 4) "Metallocene-Based Branch-Block thermoplastic Elastomers," Markel, et al. *Macromolecules* 2000, Volume 33, No. 23. pgs. 8541-8548.

Summary of the Invention

[0012] This invention relates to a polymer comprising one or more C3 to C40 olefins, optionally one or more diolefins, and less than 15 mole % of ethylene, where the polymer has:

- a) a Dot T-Peel of 1 Newton or more; and
- b) a branching index (g') of 0.95 or less measured at the Mz of the polymer;
- c) an Mw of 100,000 or less.

[0013] This invention also relates a polymer comprising one or more C3 to C40 olefins where the polymer has:

- a) a Dot T-Peel of 1 Newton or more on Kraft paper;
- b) a branching index (g') of 0.95 or less measured at the Mz of the polymer;
- c) a Mw of 10,000 to 100,000; and
- d) a heat of fusion of 1 to 70 J/g.

[0014] This invention also relates a polymer comprising one or more C3 to C40 olefins where the polymer has:

- a) a Dot T-Peel of 1 Newton or more on Kraft paper;
- b) a branching index (g') of 0.98 or less measured at the Mz of the polymer;
- c) a Mw of 10,000 to 60,000;
- d) a heat of fusion of 1 to 50 J/g.

[0015] This invention also relates to a homopolypropylene or a copolymer of propylene and up to 5 mole% ethylene having:

- a) an isotactic run length of 1 to 30 (isotactic run length "IRL" is defined to be the percent of mmmmm pentad divided by 0.5 x percent of mmmnr pentad) as determined by Carbon 13 NMR, preferably 3 to 25, more preferably 4 to 20,
- b) a percent of r dyad of greater than 20%, preferably from 20 to 70 % as determined by Carbon 13 NMR, and
- c) a heat of fusion of 70 J/g or less, preferably 60 J/g or less, more preferably between 1 and 55 J/g, more preferably between 4 and 50 J/g.

[0016] This invention further relates to a process to produce an olefin polymer comprising:

- 1) selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a crystallinity of 5% or less at selected polymerization conditions;
- 2) selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 20% or more at the selected polymerization conditions;

- 3) contacting the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, at the selected polymerization conditions in a reaction zone;
- 4) obtaining the polymer.

[0017] This invention further relates to a continuous process to produce a branched olefin polymer comprising:

- 1) selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a crystallinity of 5% or less under selected polymerization conditions;
- 2) selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 20% or more at the selected polymerization conditions;
- 3) contacting the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, and, optionally one or more diolefins;
- 4) at a temperature of greater than 100°C;
- 5) at a residence time of 120 minutes or less;
- 6) wherein the ratio of the first catalyst to the second catalyst is from 1:1 to 50:1;
- 7) wherein the activity of the catalyst components is at least 100 kilograms of polymer per gram of the catalyst components; and wherein at least 20% of the olefins are converted to polymer.

Brief Description of the Drawings

[0018] Figure 1 is an illustration of complex viscosity changes with the temperature when the samples were cooled at 10 C per minute for Examples 12, 22 and 49.

[0019] Figure 2 is a graphic illustration of the relationship between the branching index, g' , and the molecular weight for polymers produced in Examples 4 and 31.

[0020] Figure 3 is the C-13 NMR spectra of heptane soxhlet insoluble (top trace) and hexane room temperature soluble fractions (bottom trace) extracted from Example 4.

[0021] Figure 4 is the C-13 NMR spectra of aPP/scPP branch block relative to scPP and aPP control. The control samples were produced using one catalyst at a time; aPP was synthesized using a specific catalyst, while the scPP was produced using stereospecific catalyst. The top trace is the aPP control sample. The middle trace is the scPP control sample and the bottom trace is Example 4.

[0022] Figure 5 shows the relationship between temperature and complex viscosity of the fractionated samples extracted from example 31.

[0023] Figure 6 is the DSC trace for polymer of example 32 in Table 6.

Detailed Description

[0024] For the purposes of this invention and the claims thereto and for ease of reference when a polymer is referred to as comprising an olefin, the olefin present in the polymer is the polymerized form of the olefin.

[0025] In another embodiment this invention relates to a polymer comprising one or more C3 to C40 olefins, preferably propylene, and less than 50 mole % of ethylene, having:

- a) a Dot T-Peel between 1 Newton and the 10,000 Newtons; and

- b) a Mz/Mn of 2 to 200; and/or
- c) an Mw of X and a g' of Y (measured at the Mz of the polymer)
according to the following Table C:

Table C

X (Mw)	Y (g')
100,000 or less, preferably 80,000 or less, preferably 70,000 or less, more preferably 60,000 or less, more preferably 50,000 or less, more preferably 40,000 or less, more preferably 30,000 or less, more preferably 20,000 or less, more preferably 10,000 or less. In some embodiments X is also at least 7000, more preferably 10,000, more preferably at least 15,000.	0.9 or less, preferably 0.7 or less Preferably between 0.5-0.9
75,000 or less, preferably 70,000 or less, more preferably 60,000 or less, more preferably 50,000 or less, more preferably 40,000 or less, more preferably 30,000 or less, more preferably 20,000 or less, more preferably 10,000 or less. In some embodiments A is also at least 1000, preferably at least 2000, more preferably at least 3000, more preferably at least 4000, more preferably at least 5000, more preferably at least 7000, more preferably 10,000, more preferably 10,000, more preferably at least 15,000.	0.92 or less, preferably 0.6 or less preferably between 0.4-0.6-
50,000 or less, more preferably 40,000 or less, more preferably 30,000 or less, more preferably 20,000 or less, more preferably 10,000 or less. In some embodiments A is also at least 1000, preferably at least 2000, more preferably at least 3000, more preferably at least 4000, more preferably at least 5000, more preferably at least 7000, more preferably 10,000, more preferably at least 15,000.	0.95 or less, preferably 0.7 or less preferably between 0.5-0.7-
30,000 or less, preferably 25,000 or less, more preferably 20,000 or less, more preferably 15,000 or less, more preferably 10,000 or less. In some embodiments A is also at least 1000, preferably at least 2000, more preferably at least 3000, more preferably at least 4000, more preferably at least 5000, more preferably at least 7000, more preferably 10,000, more preferably at least 15,000.	0.98 or less preferably between 0.7-0.98

[0026] In another embodiment, when Mw is between 15,000 and 100,000, then
 $g' < (10^{-12} Mw^2 - 10^{-4} Mw + 1.0178)$.

[0027] In some embodiments the g' is 0.9 or less, 0.8 or less, 0.7 or less, 0.6 or less, 0.5 or less measured at the Mz of the polymer.

[0028] In another embodiment the polymer described above also has a peak melting point (Tm) between 40 and 250°C, or between 60 and 190°C, or between about 60 and 150°C, or between 80 and 130°C. In some embodiments the peak melting point is between 60 and 160°C. In other embodiments the peak melting point is between 124-140°C. In other embodiments the peak melting temperature is between 40-130°C.

[0029] In another embodiment the polymer described above also has a viscosity (also referred to a Brookfield Viscosity or Melt Viscosity) of 90,000 mPa•sec or less at 190°C (as measured by ASTM D 3236 at 190°C); or 80,000 or less, or 70,000 or less, or 60,000 or less, or 50,000 or less, or 40,000 or less, or 30,000 or less, or 20,000 or less, or 10,000 or less, or 8,000 or less, or 5000 or less, or 4000 or less, or 3000 or less, or 1500 or less, or between 250 and 6000 mPa•sec, or between 500 and 5500 mPa•sec, or between 500 and 3000 mPa•sec, or between 500 and 1500 mPa•sec, and/or a viscosity of 8000 mPa•sec or less at 160°C (as measured by ASTM D 3236 at 160°C); or 7000 or less, or 6000 or less, or 5000 or less, or 4000 or less, or 3000, or less, or 1500 or less, or between 250 and 6000 mPa•sec, or between 500 and 5500 mPa•sec, or between 500 and 3000 mPa•sec, or between 500 and 1500 mPa•sec. In other embodiments the viscosity is 200,000 mPa•sec or less at 190 ° C, depending on the application. In other embodiments the viscosity is 50,000 mPa•sec or less depending on the applications.

[0030] In another embodiment the polymer described above also has a heat of fusion of 70 J/g or less, or 60 J/g or less, or 50 J/g or less; or 40 J/g or less, or 30 J/g or less, or 20 J/g or less and greater than zero, or greater than 1 J/g, or greater than 10 J/g, or between 20 and 50 J/g.

[0031] In another embodiment the polymer described above also has a Shore A Hardness (as measured by ASTM 2240) of 95 or less, 70 or less, or 60 or less, or 50 or less, or 40 or less or 30 or less, or 20 or less. In other embodiments the Shore A Hardness is 5 or more, 10 or more, or 15 or more. In certain applications, such as packaging, the Shore A Hardness is preferably 60-70.

[0032] In another embodiment the polymer of this invention has an Mz/Mn of 2 to 200, preferably 2 to 150, preferably 10 to 100.

[0033] In another embodiment the polymer described above also has a Shear Adhesion Fail Temperature (SAFT - as measured by ASTM 4498) of 200°C or less, or of 40 to 150°C, or 60 to 130°C, or 65 to 110°C, or 70-80°C. In certain embodiments SAFT's of 130-140°C are preferred.

[0034] In another embodiment the polymer described above also has a Dot T-Peel of between 1 Newton and 10,000 Newtons, or 3 and 4000 Newtons, or between 5 and 3000 Newtons, or between 10 and 2000 Newtons, or between 15 and 1000 Newtons. Dot T-Peel is determined according to ASTM D 1876, except that the specimen is produced by combining two 1 inch by 3 inch (2.54 cm x 7.62 cm) Kraft paper substrate cut outs with a dot of adhesive with a volume that, when compressed under a 500 gram weight occupies about 1 square inch of area.(1 inch = 2.54 cm). Once made all the specimens are pulled apart in side by side testing (at a rate of 2 inches per minute) by a machine that records the destructive force of the insult being applied. The maximum force achieved for each sample tested was recorded and averaged, thus producing the Average Maximum Force which is reported as the Dot T-Peel.

[0035] In another embodiment the polymer described above also has a set time of several days to 1 second, or 60 seconds or less, or 30 seconds or less, or 20 seconds or less, or 15 seconds or less, or 10 seconds or less, or 5 seconds or less, or 4 seconds or less, or 3 seconds or less, more or 2 seconds or less, or 1 second or less.

[0036] In another embodiment the polymer described above also has an Mw/Mn of 2 to 75, or 4 to 60, or 5 to 50, or 6 to 20.

[0037] In another embodiment the polymer described above also has an Mz of 1,000,000 or less, preferably 15,000 to 1,000,000, or 20,000 to 800,000, or 25,000 to 350,000.

[0038] In another embodiment the polymer described above may also have a strain at break (as measured by ASTM D-1708 at 25 °C) of 50 to 1000%, preferably 80 to 200%. In some other embodiments the strain at break is 100 to 500%.

[0039] In another embodiment, the polymer described herein has a tensile strength at break (as measured by ASTM D-1708 at 25 °C) of 0.5 MPa or more, alternatively 0.75 MPa or more, alternatively 1.0 MPa or more, alternatively 1.5 MPa or more, alternatively 2.0 MPa or more, alternatively 2.5 MPa or more, alternatively 3.0 MPa or more, alternatively 3.5 MPa or more.

[0040] In another embodiment the polymer described above also has a crystallization point (Tc) between 20 and 110°C. In some embodiments the Tc is between 70 to 100°C. In other embodiments the Tc is between 30 to 80°C. In other embodiments the Tc is between 20 to 50°C.

[0041] In some embodiment the polymers described above has a slope of -0.1 or less, preferably -0.15 or less, more preferably -0.25 or less in the trace of complex viscosity versus temperature as shown in Figure 1 (as measured by ARES dynamic mechanical spectrometer operating at a frequency of 10 rad/s, with a strain of 20 % under a nitrogen atmosphere, and a cooling rate of 10°C/min) over the range of temperatures from Tc +10 °C to Tc+40 °C. The slope is defined as a derivative of log (complex viscosity) with respect to temperature.

[0042] In another embodiment the polymer described above has a Tc that is at least 10 °C below the Tm, preferably at least 20 °C below the Tm, preferably at least 30 °C below the Tm, more preferably at least 35 °C below the Tm.

[0043] In another embodiment some polymers described above have a melt index ratio (I_{10}/I_2) of 6.5 or less, preferably 6.0 or less, preferably 5.5 or less,

preferably 5.0 or less, preferably 4.5 or less, preferably between 1 and 6.0. (I_{10} and I_2 are measured according to ASTM 1238 D, 2.16kg, 190°C).

[0044] In another embodiment some polymers described above have a melt index (as determined by ASTM 1238 D, 2.16 kg, 190 deg. C) of 25 dg/min or more, preferably 50 dg/min or more, preferably 100 dg/min or more, more preferably 200dg/min or more, more preferably 500 dg/mn or more, more preferably 2000 dg/min or more.

[0045] In another embodiment the polymer has a melt index of 900 dg/min or more.

[0046] In another embodiment the polymer described above has a range of crystallization of 10 to 60°C wide, preferably 20 to 50 °C, preferably 30 to 45 °C in the DSC traces. In DSC traces where there are two or more non-overlapping peaks, then each peak has a range of crystallization of 10 to 60 °C wide, preferably 20 to 50 °C, preferably 30 to 45 °C in the DSC traces.

[0047] In another embodiment the polymer produced by this invention has a molecular weight distribution (Mw/Mn) of at least 2, preferably at least 5, preferably at least 10, even more preferably at least 20.

[0048] In another embodiment the polymer produced may have a unimodal, bimodal, or multimodal molecular weight distribution (Mw/Mn) distribution of polymer species as determined by Size Exclusion Chromatography (SEC). By bimodal or multimodal is meant that the SEC trace has more than one peak or inflection points. An inflection point is that point where the second derivative of the curve changes in sign (e.g., from negative to positive or vice versus).

[0049] In another embodiment the polymer described above has an Energy of activation of 8 to 15 cal/mol. Energy of activation was calculated using the relationships of complex viscosity and temperature over the region where thermal effects are responsible for viscosity increase (assuming an Arrhenius- like relationship).

[0050] In another embodiment the polymers of this invention may have a crystallinity of at least 5%.

[0051] In another embodiment the polymer described above may also have one or more of the following:

- a) a peak melting point between 60 and 190°C, or between about 60 and 150°C, or between 80 and 130°C; and/or
- b) a viscosity of 8000 mPa•sec or less at 190°C (as measured by ASTM D 3236 at 190°C); or 5000 or less, or 4000 or less, or 3000 or less, or 1500 or less, or between 250 and 6000 mPa•sec, or between 500 and 5500 mPa•sec, or between 500 and 3000 mPa•sec, or between 500 and 1500 mPa•sec, or a viscosity of 8000 mPa•sec or less at 160°C (as measured by ASTM D 3236 at 160°C); or 7000 or less, or 6000 or less, or 5000 or less, or 4000 or less, or 3000 or less, or 1500 or less, or between 250 and 6000 mPa•sec, or between 500 and 5500 mPa•sec, or between 500 and 3000 mPa•sec, or between 500 and 1500 mPa•sec; and/or
- c) an H_f (Heat of fusion) of 70 J/g or less, or 60 J/g or less, or 50 J/g or less; or 40 J/g or less, or 30 J/g or less, or 20 J/g or less and greater than zero, or greater than 1 J/g, or greater than 10 J/g, or between 20 and 50 J/g; and/or
- d) a Shore A Hardness (as measured by ASTM 2240) of 90 or less, or 80 or less, or 70 or less, or 60 or less or 50 or less, or 40 or less; and/or

- e) a Shear Adhesion Fail Temperature (SAFT - as measured by ASTM 4498) of 40 to 150°C, or 60 to 130°C, or 65 to 110°C, or 70-80°C; and/or;
- f) a Dot T-Peel of between 1 Newton and 10,000 Newtons , or 3 and 4000 Newtons, or between 5 and 3000 Newtons, or between 10 and 2000 Newtons, or between 15 and 1000 Newtons; and/or
- g) a set time of several days to 0.1 second, or 60 seconds or less, or 30 seconds or less, or 20 seconds or less, or 15 seconds or less, or 10 seconds or less, or 5 seconds or less, or 4 seconds or less, or 3 seconds or less, more or 2 seconds or less, or 1 second or less; and or
- h) an Mw/Mn of greater than 1 to 75, or 2 to 60, or 2 to 50, or 3 to 20; and/or
- i) an Mz of 1,000,000 or less, preferably 15,000 to 500,000, or 20,000 to 400,000, or 25,000 to 350,000.

[0052] Useful combinations of features include polymers as described above having a Dot T-Peel of between 1 Newton and 10,000 Newtons , or 3 and 4000 Newtons, or between 5 and 3000 Newtons, or between 10 and 2000 Newtons, or between 15 and 1000 Newtons and:

1. an Mw of 30,000 or less, a peak melting point between 60 and 190°C, a Heat of fusion of 1 to 70 J/g, a branching index (g) of 0.90 or less measured at the Mz of the polymer; and a melt viscosity of 8000 mPa•sec or less at 190°C; or
2. an Mz of 20,000 to 500,000 and a SAFT of 60 to 150°C; or
3. an Mz/Mn of 2-200 and a set time of 2 seconds or less; or
4. an H_f (heat of fusion) of 20 to 50 J/g, an Mz or 20,000-500,000 and a shore hardness of 50 or less; or
5. an Mw/Mn of greater than 1 to 50, a viscosity of 5000 or less mPa•sec at 190°C; or

6. an Mw of 50,000 or less, a peak melting point between 60 and 190°C, a heat of fusion of 2 to 70 J/g, a branching index (g') of 0.70 or less measured at the Mz of the polymer, and a melt viscosity of 8000 mPa•sec or less at 190°C.

[0053] In a preferred embodiment, the polymer of this invention comprises amorphous, crystalline and branch-block molecular structures.

[0054] In a preferred embodiment the polymer comprises at least 50 weight % propylene, preferably at least 60% propylene, alternatively at least 70% propylene, alternatively at least 80% propylene. In another embodiment the polymer comprises propylene and 15 mole % ethylene or less, preferably 10 mole % ethylene or less, more preferably 9 mole % ethylene or less, more preferably 8 mole % ethylene or less, more preferably 7 mole % ethylene or less, more preferably 6 mole % ethylene or less, more preferably 5 mole % ethylene or less, more preferably 4 mole % ethylene or less, more preferably 3 mole % ethylene or less, more preferably 2 mole % ethylene or less, more preferably 1 mole % ethylene or less.

[0055] In another embodiment the polymer of this invention comprises less than 5 mole % of ethylene, preferably less than 4.5 mole % ethylene, preferably less than 4.0 mole % ethylene, alternatively less than 3.5 mole % ethylene, alternatively less than 3.0 mole % ethylene, alternatively less than 2.5 mole % ethylene, alternatively less than 2.0 mole % ethylene, alternatively less than 1.5 mole % ethylene, alternatively less than 1.0 mole % ethylene, alternatively less than 0.5 mole % ethylene, alternatively less than 0.25 mole % ethylene, alternatively 0 mole % ethylene.

[0056] In another embodiment the polymer produced has a glass transition temperature (Tg) as measured by ASTM E 1356 of 5°C or less, preferably 0°C or

less, preferably -5 °C or less, alternatively between -5°C and -40°C, alternatively between -5 °C and -15°C.

[0057] In another embodiment the polymer of this invention has an amorphous content of at least 50%, alternatively at least 60%, alternatively at least 70 %, even alternatively between 50 and 99%. Percent amorphous content is determined using Differential Scanning Calorimetry measurement according to ASTM E 794-85.

[0058] In another embodiment the polymer of this invention has a crystallinity of 40 % or less, alternatively 30% or less, alternatively 20% or less, even alternatively between 10% and 30%. Percent crystallinity content is determined using Differential Scanning Calorimetry measurement according to ASTM E 794-85. In another embodiment, the polymers described herein have a percent crystallinity of between 5 and 40 %, alternatively between 10 to 30 %.

[0059] In another embodiment the polymer produced by this invention has a molecular weight distribution (Mw/Mn) of at least 1.5, preferably at least 2, preferably at least 5, preferably at least 10, even alternatively at least 20. In other embodiments the Mw/Mn is 20 or less, 10 or less, even 5 or less. Molecular weight distribution generally depends on the catalysts used and process conditions such as temperature, monomer concentration, catalyst ratio, if multiple catalysts are used, and the presence or absence of hydrogen. Hydrogen may be used at amounts up to 2 weight %, but is preferably used at levels of 50 to 500 ppm.

[0060] In another embodiment the polymer produced is found to have at least two molecular weights fractions are present at greater than 2 weight %, preferably greater than 20 weight %, each based upon the weight of the polymer as measured by Gel Permeation Chromatography. The fractions can be identified on the GPC trace by observing two distinct populations of molecular weights. An

example would be a GPC trace showing a peak at 20,000 Mw and another peak at 50,000 Mw where the area under the first peak represents more than 2 weight % of the polymer and the area under the second peak represents more than 2 weight % of the polymer.

[0061] In another embodiment the polymer of this invention has 20 weight % or more (based upon the weight of the starting polymer) of hexane room temperature soluble fraction, and 70 weight % or less, preferably 50 weight% or less of Soxhlet boiling heptane insolubles, based upon the weight of the polymer. Soxhlet heptane insoluble refers to one of the fractions obtained when a sample is fractionated using successive solvent extraction technique. The fractionations are carried out in two steps: one involves room temperature solvent extraction, the other soxhlet extraction. In the room temperature solvent extraction, about one gram of polymer is dissolved in 50 ml of solvent (e.g., hexane) to isolate the amorphous or very low molecular weight polymer species. The mixture is stirred at room temperature for about 12 hours. The soluble fraction is separated from the insoluble material using filtration under vacuum. The insoluble material is then subjected to a Soxhlet extraction procedure. This involves the separation of polymer fractions based on their solubility in various solvents having boiling points from just above room temperature to 110°C. The insoluble material from the room temperature solvent extraction is first extracted overnight with a solvent such as hexane and heptane (Soxhlet); the extracted material is recovered by evaporating the solvent and weighing the residue. The insoluble sample is then extracted with a solvent having higher boiling temperature such as heptane and after solvent evaporation, it is weighed. The insolubles and the thimble from the final stage are air-dried in a hood to evaporate most of the solvent, then dried in a nitrogen-purged vacuum oven. The amount of insoluble left in the thimble is then calculated, provided the tare weight of the thimble is known.

[0062] In another embodiment, the polymers produced in this invention have a heptane insoluble fraction 70 weight% or less, based upon the weight of the starting polymer, and the heptane insoluble fraction has branching index g' of 0.9 (preferably 0.7) or less as measured at the M_2 of the polymer. In a preferred embodiment the composition also has at least 20 weight% hexane soluble fraction, based upon the weight of the starting polymer. In another embodiment, the polymers produced in this invention have a heptane insoluble fraction 70 weight% or less, based upon the weight of the starting polymer and a M_2 between 20,000 and 5000,000 of the heptane insoluble portion. In a preferred embodiment the composition also has at least 20 weight% hexane soluble fraction, based upon the weight of the starting polymer. In another embodiment the polymers produced have a hexane soluble portion of at least 20 weight %, based upon the weight of the starting polymer.

[0063] In another embodiment the polymer comprises propylene and 15 mole % ethylene or less, preferably 10 mole % ethylene or less, more preferably 9 mole % ethylene or less, more preferably 8 mole % ethylene or less, more preferably 7 mole % ethylene or less, more preferably 6 mole % ethylene or less, more preferably 5 mole % ethylene or less, more preferably 4 mole % ethylene or less, more preferably 3 mole % ethylene or less, more preferably 2 mole % ethylene or less, more preferably 1 mole % ethylene or less.

[0064] In another embodiment the polymer of this invention comprises less than 5 mole % of ethylene, preferably less than 4.5 mole % ethylene, preferably less than 4.0 mole % ethylene, alternatively less than 3.5 mole % ethylene, alternatively less than 3.0 mole % ethylene, alternatively less than 2.5 mole % ethylene, alternatively less than 2.0 mole % ethylene, alternatively less than 1.5 mole % ethylene, alternatively less than 1.0 mole % ethylene, alternatively less than 0.5 mole % ethylene, alternatively less than 0.25 mole % ethylene, alternatively 0 mole % ethylene.

[0065] For ease of reference the polymer produced by the second catalyst having at least 20% crystallinity may also be referred to as the "semi-crystalline polymer" and the polymer produced by the first catalyst component having a crystallinity of less than 5% may be referred to as the "amorphous polymer."

[0066] In another embodiment of this invention the polymer produced has a characteristic three-zone complex viscosity-temperature pattern, as shown in Figure 1. The temperature dependence of complex viscosity was measured using ARES dynamic mechanical spectrometer operating at a frequency of 10 rad/s, with a strain of 20 % under a nitrogen atmosphere, and a cooling rate of 10°C/min. The sample was first molten then gradually cooled down to room temperature while monitoring the build-up in complex viscosity. Above the melting point, which is typical of polymer processing temperature, the complex viscosity is relatively low (Zone I) and increases gradually with decreasing temperature. In zone II, a sharp increase in complex viscosity appears as temperature is dropped. The third zone (Zone III) is the high complex viscosity zone, which appears at lower temperatures corresponding to application (end use) temperatures. In Zone III the complex viscosity is high and varies slightly with further decrease in temperature. Such a complex viscosity profile provides, in hot melt adhesive applications, a desirable combination of long opening time at processing temperatures and fast set time at lower temperatures.

[0067] In a preferred embodiment, the polymers produced herein having less than 1 mol % ethylene, have at least 2 mol% $(\text{CH}_2)_2$ units, preferably 4 mol%, preferably 6 mol%, more preferably 8 mol%, more preferably 10 mol%, more preferably 12 mol%, more preferably 15 mol%, more preferably 18 mol%, more preferably 5 mol% as measured by Carbon 13 NMR as described below.

[0068] In another embodiment, the polymers produced herein having between 1 and 10 mol % ethylene, have at least 2 +X mol% $(\text{CH}_2)_2$ units,

preferably 4 +X mol%, preferably 6 +X mol%, more preferably 8 +X mol%, more preferably 10+X mol%, more preferably 12 +X mol%, more preferably 15 +X mol%, more preferably 18 +X mol%, more preferably 20 +X mol%, where X is the mole % of ethylene, and the $(\text{CH}_2)_2$ units are determined by Carbon 13 NMR as described below.

[0069] In a preferred embodiment, the polymers produced herein, having less than 1 mol% ethylene, have an amorphous component (which is defined to be that portion of the polymer composition that has a crystallinity of less than 5%) which contains at least 3 mol% $(\text{CH}_2)_2$ units, preferably 4 mol%, preferably 6 mol%, more preferably 8 mol%, more preferably 10 mol%, more preferably 12 mol%, more preferably 15 mol%, more preferably 18 mol%, more preferably 20 mol% as measured by Carbon 13 NMR as described below.

[0070] In an another embodiment, the polymers produced herein having between 1 and 10 mol % ethylene, have an amorphous component (which is defined to be that portion of the polymer composition that has a crystallinity of less than 20%) which contains at least 3 +X mol% $(\text{CH}_2)_2$ units, preferably 4 +X mol%, preferably 6 +X mol%, more preferably 8 +X mol%, more preferably 10+X mol%, more preferably 12 +X mol%, more preferably 15 +X mol%, more preferably 18 +X mol%, more preferably 20 +X mol%, where X is the mole % of ethylene, and the $(\text{CH}_2)_2$ units are determined by Carbon 13 NMR as described below.

Monomers

[0071] In a preferred embodiment the polymer comprises an olefin homopolymer or copolymer, comprising one or more C3 to C40 alpha olefins. In another preferred embodiment the olefin polymer further comprises one or more diolefin comonomers, preferably one or more C4 to C40 diolefins.

[0072] In a preferred embodiment the polymer comprises an olefin homopolymer or copolymer, having less than 5 mol% ethylene, and comprising one or more C3 to C40 alpha olefins. In another preferred embodiment the olefin polymer, having less than 5 mol% ethylene, further comprises one or more diolefin comonomers, preferably one or more C4 to C40 diolefins.

[0073] In a preferred embodiment the polymer produced herein is a propylene homopolymer or copolymer. The comonomer is preferably a C4 to C20 linear, branched or cyclic monomer, and in one embodiment is a C4 to C12 linear or branched alpha-olefin, preferably butene, pentene, hexene, heptene, octene, nonene, decene, dodecene, 4-methyl-pentene-1, 3-methyl pentene-1, 3,5,5-trimethyl-hexene-1, and the like. Ethylene may be present at 5 mol% or less.

[0074] In another embodiment the polymer produced herein is a copolymer of one or more linear or branched C3 to C30 prochiral alpha-olefins or C5 to C30 ring containing olefins or combinations thereof capable of being polymerized by either stereospecific and non-stereospecific catalysts. Prochiral, as used herein, refers to monomers that favor the formation of isotactic or syndiotactic polymer when polymerized using stereospecific catalyst(s).

[0075] The polymerizable olefinic moiety can be linear, branched, cyclic-containing, or a mixture of these structures. Preferred linear alpha-olefins include C3 to C8 alpha-olefins, more preferably propylene, 1-butene, 1-hexene, and 1-octene, even more preferably propylene or 1-butene. Preferred branched alpha-olefins include 4-methyl-1-pentene, 3-methyl-1-pentene, and 3,5,5-trimethyl-1-hexene, 5-ethyl-1-nonene. Preferred aromatic-group-containing monomers contain up to 30 carbon atoms. Suitable aromatic-group-containing monomers comprise at least one aromatic structure, preferably from one to three, more preferably a phenyl, indenyl, fluorenyl, or naphthyl moiety. The aromatic-group-

containing monomer further comprises at least one polymerizable double bond such that after polymerization, the aromatic structure will be pendant from the polymer backbone. The aromatic-group containing monomer may further be substituted with one or more hydrocarbyl groups including but not limited to C1 to C10 alkyl groups. Additionally two adjacent substitutions may be joined to form a ring structure. Preferred aromatic-group-containing monomers contain at least one aromatic structure appended to a polymerizable olefinic moiety. Particularly preferred aromatic monomers include styrene, alpha-methylstyrene, para-alkylstyrenes, vinyltoluenes, vinylnaphthalene, allyl benzene, and indene, especially styrene, paramethyl styrene, 4-phenyl-1-butene and allyl benzene.

[0076] Non aromatic cyclic group containing monomers are also preferred. These monomers can contain up to 30 carbon atoms. Suitable non-aromatic cyclic group containing monomers preferably have at least one polymerizable olefinic group that is either pendant on the cyclic structure or is part of the cyclic structure. The cyclic structure may also be further substituted by one or more hydrocarbyl groups such as, but not limited to, C1 to C10 alkyl groups. Preferred non-aromatic cyclic group containing monomers include vinylcyclohexane, vinylcyclohexene, vinylnorbornene, ethylidene norbornene, cyclopentadiene, cyclopentene, cyclohexene, cyclobutene, vinyladamantane and the like.

[0077] Preferred diolefin monomers useful in this invention include any hydrocarbon structure, preferably C4 to C30, having at least two unsaturated bonds, wherein at least two of the unsaturated bonds are readily incorporated into a polymer by either a stereospecific or a non-stereospecific catalyst(s). It is further preferred that the diolefin monomers be selected from alpha, omega-diene monomers (i.e., di-vinyl monomers). More preferably, the diolefin monomers are linear di-vinyl monomers, most preferably those containing from 4 to 30 carbon atoms. Examples of preferred dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene,

tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, hencicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (Mw less than 1000 g/mol). Preferred cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethyldene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

[0078] In a preferred embodiment one or more dienes are present in the polymer produced herein at up to 10 weight %, preferably at 0.00001 to 1.0 weight %, preferably 0.002 to 0.5 weight %, even more preferably 0.003 to 0.2 weight %, based upon the total weight of the composition. In some embodiments 500 ppm or less of diene is added to the polymerization, preferably 400 ppm or less, preferably or 300 ppm or less. In other embodiments at least 50 ppm of diene is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

[0079] In a preferred embodiment the olefin polymer is homopolypropylene. In another preferred embodiment the olefin polymer comprises propylene, ethylene, preferably less than 5 mol% ethylene, and at least one divinyl comonomer. In another preferred embodiment the olefin polymer comprises propylene and at least one divinyl comonomer.

[0080] In another embodiment, the olefin polymer comprises:
a first monomer present at from 40 to 95 mole %, preferably 50 to 90 mole %, preferably 60 to 80 mole %, and
a comonomer present at from 5 to 40 mole %, preferably 10 to 60 mole %, more preferably 20 to 40 mole %, and

a termonomer present at from 0 to 10 mole%, more preferably from 0.5 to 5 mole%, more preferably 1 to 3 mole %.

[0081] In a preferred embodiment the first monomer comprises one or more of any C3 to C8 linear, branched or cyclic alpha-olefins, including propylene, butene (and all isomers thereof), pentene (and all isomers thereof), hexene (and all isomers thereof), heptene (and all isomers thereof), and octene (and all isomers thereof). Preferred monomers include propylene, 1-butene, 1-hexene, 1-octene, and the like.

[0082] In a preferred embodiment the comonomer comprises one or more of any C2 to C40 linear, branched or cyclic alpha-olefins (provided ethylene, if present, is present at 5 mole% or less), including ethylene, propylene, butene, pentene, hexene, heptene, and octene, nonene, decene, undecene, dodecene, hexadecene, styrene, 3,5,5- trimethylhexene-1, 3-methylpentene-1, 4-methylpentene-1, norbornene and cyclopentene.

[0083] In a preferred embodiment the termonomer comprises one or more of any C2 to C40 linear, branched or cyclic alpha-olefins, (preferably ethylene, if present, is present at 5 mole% or less), including, but not limited to, ethylene, propylene, butene, pentene, hexene, heptene, and octene, nonene, decene, undecene, dodecene, hexadecene, butadiene, 1,5-hexadiene, 1,6-heptadiene, 1,4-pentadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,11-dodecadiene, styrene, 3,5,5-trimethylhexene-1, 3-methylpentene-1, 4-methylpentene-1, and cyclopentadiene.

[0084] In a preferred embodiment the polymer comprises propylene and from 0 to 50 mole % ethylene, preferably from 0 to 30 mole % ethylene, more preferably from 0 to 15 mole % ethylene, more preferably from 0 to 10 mole % ethylene, more preferably from 0 to 5 mole % ethylene.

[0085] In a preferred embodiment the polymer comprises propylene and from 0 to 50 mole % butene, preferably from 0 to 30 mole % butene, more preferably from 0 to 15 mole % butene, more preferably from 0 to 10 mole % butene, more preferably from 0 to 5 mole % butene.

[0086] In a preferred embodiment the polymer comprises propylene and from 0 to 50 mole % hexene, preferably from 0 to 30 mole % hexene, more preferably from 0 to 15 mole % hexene, more preferably from 0 to 10 mole % hexene, more preferably from 0 to 5 mole % hexene.

Process

[0087] This invention further relates to a process to produce the olefin polymers described above comprising:

- 1) selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a heat of fusion of 10 J/g or less;
- 2) selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 20% or more;
- 3) contacting the catalyst components in the presence of one or more activators with one or more olefins, in a reaction zone.

[0088] This invention further relates to a process to produce the olefin polymers described above comprising:

- 1) selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a heat of fusion of 10 J/g or less;

- 2) selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 20% or more;
- 3) contacting the catalyst components in the presence of one or more activators with one or more olefins and one or more dienes, in a reaction zone.

[0089] This invention further relates to a process to produce the olefin polymers described above comprising:

- 1) selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less and a heat of fusion of 70 J/g or less, capable of polymerizing macromonomers having reactive termini;
- 2) selecting a second catalyst component capable of producing macromonomers having reactive termini, an Mw of 100,000 or less and a crystallinity of 30% or more;
- 3) contacting the catalyst components in the presence of one or more activators with one or more olefins, and optionally a diolefin in a reaction zone.

[0090] This invention further relates to a process to produce the olefin polymers described above comprising:

- 1) selecting a first catalyst component capable of producing a polymer having an Mw of 30,000 or less and a heat of fusion of 10 J/g or less, capable of polymerizing macromonomers having reactive termini;
- 2) selecting a second catalyst component capable of producing macromonomers having reactive termini, an Mw of 30,000 or less and a crystallinity of 20% or more;

- 3) contacting the catalyst components in the presence of one or more activators with propylene, and optionally other olefins, in a reaction zone

[0091] In another preferred embodiment this invention relates to a continuous process to produce a branched olefin polymer comprising:

- 1) selecting a first catalyst component capable of producing a polymer having an Mw of 100,000 or less, preferably 80,000 or less, preferably 60,000 or less and a crystallinity of 5% or less, preferably 3% or less, more preferably 2% or less, under selected polymerization conditions;
- 2) selecting a second catalyst component capable of producing polymer having an Mw of 100,000 or less, preferably 80,000 or less, preferably 60,000 or less and a crystallinity of 20% or more, preferably 30% or more, more preferably 40% or more at the selected polymerization conditions;
- 3) contacting, under the selected polymerization conditions, the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, preferably one or more C3 to C12 olefins, preferably C3 and one or more of ethylene and/or C4 to C20 comonomers, and, optionally one or more diolefins, preferably a C4 to C20 diene;
- 4) at a temperature of greater than 70 °C, preferably greater than 100°C, preferably greater than 105°C, more preferably greater than 110°C, more preferably greater than 115°C ;
- 5) at a residence time of 120 minutes or less, preferably 60 minutes or less, preferably 50 minutes or less, preferably 40 minutes, preferably 30 minutes or less, preferably 25 minutes or less, more preferably 20 minutes or less, more preferably 15 minutes or less, more preferably at 10 minutes or less, more preferably at 5 minutes

or less, more preferably at 3 minutes or less, alternately the residence time may be between 60 and 120 minutes;

- 6) wherein the ratio of the first catalyst to the second catalyst is from 1:1 to 50:1, preferably 1:1 to 20:1, more preferably 1:1 to 1:10;
- 7) wherein the activity of the catalyst components is at least 3 kilograms, preferably at least 50 kilograms, more preferably at least 100 kilograms, more preferably at least 200 kilograms, more preferably, 300 kilograms, more preferably 400 kilograms, more preferably 500 kilograms of polymer per gram of the catalyst mixture; and wherein at least 80%, preferably at least 85%, more preferably at least 90%, more preferably at least 95 % of the olefins are converted to polymer.

[0092] In another embodiment the a first catalyst component is capable of producing a polymer having an Mw of 100,000 or less and a crystallinity of 5% or less at selected polymerization conditions and the second catalyst component is capable of producing polymer having an Mw of 100,000 or less and a crystallinity of 20% or more at the selected polymerization conditions.

[0093] In another embodiment at least 20 % or more of the olefins are converted to polymer, preferably 20% or more, more preferably 60% or more, more preferably 75% or more, more preferably 85% or more, more preferably 95% or more.

[0094] In a preferred embodiment the process described above takes place in a solution phase, slurry or bulk phase polymerization process.

[0095] By continuous is meant a system that operates (or is intended to operate) without interruption or cessation. For example a continuous process to

produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn.

[0096] In another preferred embodiment, in the process described above the concentrations of the reactants vary by 20% or less in the reaction zone during the residence time, preferably by 15% or less, more preferably by 10% or less. In a preferred embodiment the concentration of the monomer(s) remains constant in the reaction zone during the residence time. Preferably the concentration of the monomer(s) varies by 20% or less, preferably by 15% or less, more preferably by 10% or less, more preferably by 5% or less.

[0097] In a preferred embodiment the concentration of the catalyst components remains constant in the reaction zone during the residence time. Preferably the concentration of the monomer(s) varies by 20% or less, preferably by 15% or less, more preferably by 10% or less, more preferably by 5% or less.

[0098] In a preferred embodiment the concentration of the activator(s) remains constant in the reaction zone during the residence time. Preferably the concentration of the monomer(s) varies by 20% or less, preferably by 15% or less, more preferably by 10% or less, more preferably by 5% or less.

[0099] In another preferred embodiment a third catalyst (or more) may be present in the processes described above. The third catalyst may be any of the catalyst components listed herein. Preferred third catalysts include catalysts that are capable of producing waxes. Other preferred third catalysts may include any catalyst described herein. One may select two or more catalysts to produce various macromonomers having reactive termini, used in combination with a catalyst that can polymerize such macromonomers. One may select two or more catalysts that can polymerize macromonomers and one catalyst that can produce macromonomers with reactive termini. Likewise one could also select three

catalysts that produce different polymers under the same reaction conditions. For example one could select a catalyst that produces a somewhat crystalline polymer, one that produces a very crystalline polymer and one that produces an amorphous polymer, any of which may produce macromonomers with reactive termini or polymerize polymers having reactive termini. Similarly one could select two catalysts, one that produces crystalline polymers and one that produces an amorphous polymer, any of which may make macromonomers with reactive termini or polymerize polymers having reactive termini. Likewise one could select a catalyst that produces a somewhat crystalline polymer, one that produces a wax and one that produces an amorphous polymer, any of which may make macromonomers with reactive termini or polymerize polymers having reactive termini.

[00100] By reaction zone is meant an area where the activated catalyst and monomers can react.

[00101] By macromonomers having reactive termini is meant a polymer having twelve or more carbon atoms (preferably 20 or more, more preferably 30 or more, more preferably between 12 and 8000 carbon atoms) and having a vinyl, vinylidene, vinylene or other terminal group that can be polymerized into a growing polymer chain. By capable of polymerizing macromonomer having reactive termini is meant a catalyst component that can incorporate a macromonomer (which tend to be molecules larger than a typical single monomer such as ethylene or propylene), having reactive termini into a growing polymer chain. Vinyl terminated chains are generally more reactive than vinylene or vinylidene terminated chains.

[00102] In a particular embodiment the present invention is directed to a polyolefin polymer produced by copolymerizing one or more C₃ or higher alpha-olefins and/or one or more di-vinyl monomers, and optionally up to 5 mol%

ethylene, in the presence of at least one stereospecific catalyst system and at least one other catalyst system in the same polymerization medium. Preferably, the polymerizations are carried out simultaneously in the presence of both catalysts. The polymer so produced may contain amorphous polymer segments and crystalline polymer segments in which at least some of the segments are linked. Typically the amorphous and the crystalline polymer segments are copolymers of one or more alpha-olefins (optionally including up to 5 mol% ethylene) and/or one or more monomers having at least two olefinically unsaturated bonds. Both of these unsaturated bonds are suitable for and readily incorporated into a growing polymer chain by coordination polymerization using either the first or second catalyst systems independently such that the di-olefin is incorporated into polymer segments produced by both catalysts in the mixed catalyst system according to this invention. In a preferred embodiment these monomers having at least two olefinically unsaturated bonds are di-olefins, preferably di-vinyl monomers. Crosslinking of at least a portion of the mixture of polymer segments is believed to be accomplished during the polymerization of the composition by incorporation of a portion of di-vinyl comonomers into two polymer segments, thus producing a crosslink between those segments.

[00103] In another embodiment, polyolefin branch-block compositions containing amorphous and semi-crystalline components may be prepared in a single reactor to yield desired property balance. In particular, aPP-g-scPP branch structures may be produced in-situ in a continuous solution reactor using mixed catalysts and propylene as the preferred feed. In one embodiment stereospecific bridged bis-indenyl group 4 catalysts can be selected to produce semicrystalline PP macromonomers. (All references to the Periodic Table of the Elements are to the Table published in Chemical and Engineering News, 63(5), 27, 1985.) A bridged mono-cyclopentadienyl heteroatom group 4 catalyst can be used to build amorphous PP (aPP) backbone while simultaneously incorporating some of the semi-crystalline macromonomers (scPP). This is believed to produce aPP-g-

scPP structure where the "-g-" indicates that the polymer types are at least partially grafted. By selecting the catalysts, the polymerization reaction conditions, and/or by introducing a diene modifier, the amorphous and crystalline components can be linked together to produce various branch-block structures. To effectively incorporate into a growing chain, a macromonomer with vinyl end group is preferred. Other types of chain end unsaturations (vinylene and vinylidene) can also be used. While not wishing to be bound by theory, branch-block copolymer is believed to comprise an amorphous backbone having crystalline side chains originating from the scPP macromonomers and the sidechains are believed to be polypropylene macromonomers, which can be prepared under solution polymerization conditions with catalysts suitable for preparing either of isotactic or syndiotactic polypropylene.

[00104] A preferred reaction process to produce polypropylene macromonomers having high levels of terminal vinyl unsaturation is described in U.S. patent 6,117,962. Typically used catalysts are stereorigid, chiral or asymmetric, bridged metallocenes. See, for example, U.S. Pat. No. 4,892,851, U.S. Pat. No. 5,017,714, U.S. Pat. No. 5,132,281, U.S. Pat. No. 5,296,434, U.S. Pat. No. 5,278,264, U.S. Pat. No. 5,304,614, U.S. Pat. No. 5,510,502, WO-A-(PCT/US92/10066) WO-A- 93/19103, EP-A2-0 577 581, EP-A1-0 578 838, and academic literature "The Influence of Aromatic Substituents on the Polymerization Behavior of Bridged Zirconocene Catalysts", Spaleck, W., et al., Organometallics 1994, 13, 954-963, and "ansa-Zirconocene Polymerization Catalysts with Annulated Ring Ligands-Effects on Catalytic Activity and Polymer Chain Lengths", Brinzingier, H., et al, Organometallics 1994, 13, 964-970, and documents referred to therein.

[00105] In some embodiments, the first catalyst which comprises a stereorigid transition metal pre-catalyst compound used to produce the semi-crystalline polypropylene macromonomers of the present invention is selected

from the group consisting of racemic bridged bis(indenyl) zirconocenes or hafnocenes. In another embodiment, the transition metal pre-catalyst compound is a rac-dimethylsilyl-bridged bis(indenyl) zirconocene or hafnocene. In another embodiment, the transition metal pre-catalyst compound is rac-dimethylsilyl bis(2-methyl-4-phenylindenyl) zirconium or hafnium dichloride or dimethyl. In another preferred embodiment, the transition metal catalyst is a rac-dimethylsilyl-bridged bis(indenyl) hafnocene such as rac-dimethylsilyl bis(indenyl)hafnium dimethyl or dichloride.

[00106] It is believed that the fraction of branch-block and the level of branching depend on the availability of macromonomers with unsaturated chain end and macromonomer incorporation capability of the specific catalyst. To increase the population of aPP-g-scPP branch-block composition, one typically operates within a process window that favors macromonomer production and insertion. Such conditions have been described in U.S. patent 6,117,962 and the journal article by W. Weng et al., *Macromol. Rapid Commun.*, 2000, 21, 1103-1107 and are further illustrated by the examples therein.

[00107] It is also believed that the higher the population of vinyl terminated scPP macromonomers the higher the probability of getting them incorporated into aPP backbone and therefore the higher the branch-block population.

[00108] To further increase the population of macromonomers having vinyl chain ends diolefin monomers can be introduced into the reaction medium. The resultant product is typically a blend comprised of isotactic polypropylene segments, atactic polypropylene segments, and increased population of branch-block species resulting from the additional couplings brought about by the diolefin crosslinking agent.

[00109] Crosslinking typically refers to the connection of two polymer segments by incorporation of each double bond of a diolefin monomer into two different polymer segments. The polymer segments so connected can be the same or different, with respect to their crystallinity. Three or more polymer segments may also be connected via incorporation of two or more diolefins in one polymer segment into two other polymer segments.

[00110] A consideration for selection of the monomer, or combinations of monomers, is that, both crystalline and amorphous polymer segments can be formed with the selection of two or more different catalyst systems. In some embodiments it is further desired that the level of incorporation of the diolefin monomer, if present, into the crystalline segments be limited to an amount that will not substantially alter its crystallinity. The diolefin coupling agent is typically kept minimum to insure the overall composition has a viscosity of 8000 mPa•s or less for some adhesive applications.

[00111] As mentioned above, to increase the population of aPP-g-scPP branch-block composition, one typically operates within a process window that favors macromonomer production and insertion. Favorable conditions include:

- 1) High concentration of catalyst producing the semi-crystalline vinyl terminated macromonomers, and or
- 2) Adjusting the Al/metal ratio; and or
- 3) High operating temperature; and or
- 4) Catalyst structure that has a high affinity for macromonomer incorporation; and or
- 5) Relatively long residence time; and or
- 6) High monomer conversion (monomer starvation condition enhances the insertion of macromonomer); and or

7) Addition of modifier (diene) to enhance the population of vinyl terminated macromonomers.

[00112] Another method of enhancing aPP-g-scPP branch block compositions is to add in a chain transfer agent that transfers a vinyl group to the end of the polymer chain while deactivating the catalyst. Such chain transfer agents include, but are not limited to, vinyl chloride, vinyl fluoride, vinyl bromide. In the process, the catalyst is reactivated by the presence of an aluminum alkyl activator such as an alumoxane (typically methylalumoxane).

[00113] Similarly, melting and crystallization characteristics can be controlled through catalyst selection, comonomer addition and changes in process conditions such as temperature and catalyst ratio if more than one catalyst is used.

Catalyst Compounds

[00114] Any catalyst compound that can produce the desired polymer species may be used in the practice of this invention. In the description herein the transition metal compound may be described as a catalyst precursor, a pre-catalyst compound or a catalyst compound, and these terms are used interchangeably. A catalyst system is combination of a catalyst precursor and an activator.

Catalyst Compounds and Selection

[00115] Any pre-catalyst compound (catalyst precursor compound) that can produce the desired polymer species may be used in the practice of this invention. Pre-catalyst compounds which may be utilized in the process of the invention include metallocene transition metal compounds (containing one, two, or three cyclopentadienyl ligands per metal atom), non-metallocene early transition metal

compounds (including those with amide and/or phenoxide type ligands), non-metallocene late transition metal compounds (including those with diimine or diiminepyridyl ligands), and other transition metal compounds.

[00116] Generally, bulky ligand metallocene compounds (pre-catalysts) useful in this invention include half and full sandwich compounds having one or more bulky ligands bonded to at least one metal atom. Typical bulky ligand metallocene compounds are generally described as containing one or more bulky ligand(s) and one or more leaving group(s) bonded to at least one metal atom. The bulky ligands are generally represented by one or more open, acyclic, or fused ring(s) or ring system(s) or a combination thereof. These bulky ligands, preferably the ring(s) or ring system(s) are typically composed of atoms selected from Groups 13 to 16 atoms of the Periodic Table of Elements, preferably the atoms are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum or a combination thereof. Most preferably, the ring(s) or ring system(s) are composed of carbon atoms such as but not limited to those cyclopentadienyl ligands or cyclopentadienyl-type ligand structures or other similar functioning ligand structure such as a pentadienyl, a cyclooctatetraenyl, a cyclobutadienyl, or a substituted allyl ligand. Other ligands that can function similarly to a cyclopentadienyl-type ligand include amides, phosphides, imines, phosphinimines, amidinates, and ortho-substituted phenoxides. The metal atom is preferably selected from Groups 3 through 15 and or lanthanide or actinide series of the Periodic Table of Elements. Preferably the metal is a transition metal from Groups 3 through 12, more preferably Groups 4, 5 and 6, and most preferably the transition metal is from Group 4.

[00117] In one embodiment, the catalyst composition useful in the invention includes one or more bulky ligand metallocene catalyst compounds represented by the formula:



where M is a metal atom from the Periodic Table of the Elements and may be a Group 3 to 12 metal or from the lanthanide or actinide series of the Periodic Table of Elements, preferably M is a Group 4, 5 or 6 transition metal, more preferably M is a Group 4 transition metal, even more preferably M is zirconium, hafnium or titanium. The bulky ligands, L^A and L^B , are open, acyclic or fused ring(s) or ring system(s) and are any ancillary ligand system, including unsubstituted or substituted, cyclopentadienyl ligands or cyclopentadienyl-type ligands, heteroatom substituted and/or heteroatom containing cyclopentadienyl-type ligands. Non-limiting examples of bulky ligands include cyclopentadienyl ligands, cyclopentaphenanthrenyl ligands, indenyl ligands, benzindenyl ligands, fluorenyl ligands, dibenzo[b,h]fluorenyl ligands, benzo[b]fluorenyl ligands, cyclooctatetraenyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, phosphinimine (WO 99/40125), pyrrolyl ligands, pyrozoyl ligands, carbazoyl ligands, boratobenzene ligands and the like, including hydrogenated versions thereof, for example tetrahydroindenyl ligands. In one embodiment, L^A and L^B may be any other ligand structure capable of π -bonding to M. In yet another embodiment, the atomic molecular weight (MW) of L^A or L^B exceeds 60 a.m.u., preferably greater than 65 a.m.u. In another embodiment, L^A and L^B may comprise one or more heteroatoms, for example, nitrogen, silicon, boron, germanium, sulfur and phosphorous, in combination with carbon atoms to form an open, acyclic, or preferably a fused, ring or ring system, for example, a hetero-cyclopentadienyl ancillary ligand. Other L^A and L^B bulky ligands include but are not limited to bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borolides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles. Independently, each L^A and L^B may be the same or different type of bulky ligand